# Design, synthesis and characterization of luminescent organic semiconductors

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# Introduction

## 1.1 Conjugated polymers

In recent years, an enormous interest in conjugated polymers has developed, mainly as a result of the possibility to combine their semiconducting properties with classical polymer properties such as flexibility, low weight and processability [1-3]. In the context of semiconductor devices, the main interest lies in the fabrication of thin-film devices over large areas, which has been proven difficult to achieve with most inorganic materials [4]. Conjugated polymers can be recognized by the alternation of double and single bonds along the chain. Their semiconducting properties arise from delocalization of $\pi$ bonding and $\pi^*$ antibonding molecular orbitals along the chain. While the first conjugated polymers were characterized 25 years ago, as a class (Figure 1.1), they continue to produce novel materials with new and potentially useful physical properties. The challenge for chemists and materials scientists is to develop materials and techniques to match the properties of these organic semiconductors to the desired applications.

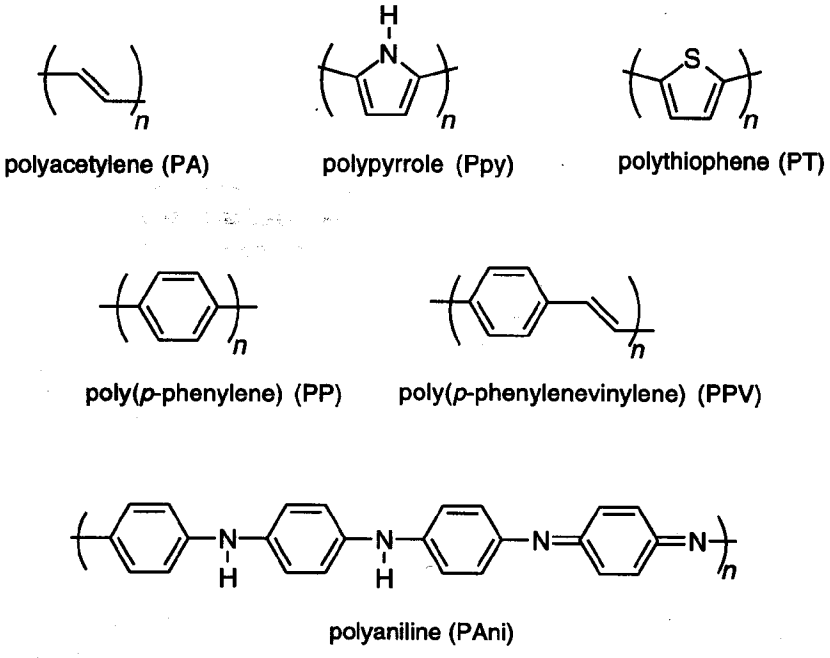



**Figure 1.1** *Conjugated polymers for (semi-)conductor applications.*

Originally, the interest in conjugated polymers arose from the possibility to make them good electrical conductors upon doping [5-7]. Since the late 1980's, however, the device physics of the pure materials has attracted attention, since they were found to be applicable as the active semiconductor elements in field-effect transistors [8-11] and, more recently, in light-emitting diodes [12-16].

## 1.2 Excitations in organic molecules

Large conjugated molecules have HOMO-LUMO gaps well within the semiconductor range of 1-4 eV (1240-310 nm), which spans the range from the infrared to the ultraviolet and includes the all-important visible region of the spectrum (HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital). Excitation results in a local deformation of the molecule around the site of electronic excitation [17-19]. The change in chain geometry (from aromatic towards quinoid) has the effect of pulling levels away from the band edges into the gap: rather than exciting an electron from a highly delocalized, fully occupied molecular orbital to another delocalized empty orbital, two, much more localized levels are eventually created within the gap (Figure 1.2). The degree of (de)localization is likely to depend on the nature of the conjugated system. Aromatic rings tend to localize the excitation because the alternative electronic configuration, the quinoid one, is higher in energy.

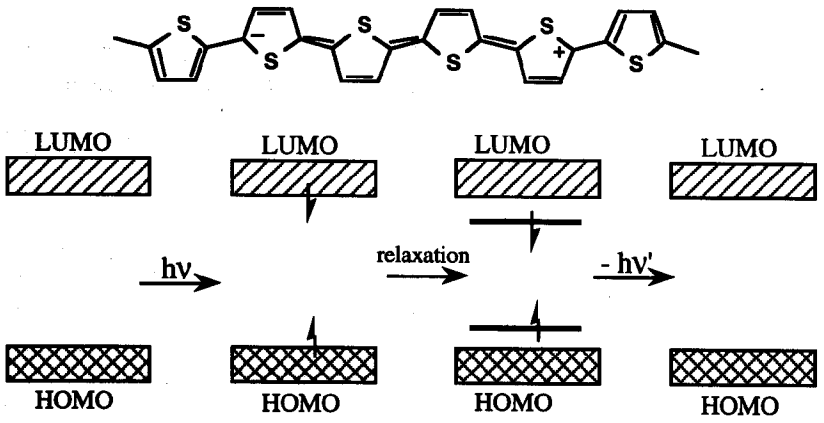



**Figure 1.2** *Schematic diagram showing radiative decay of a singlet exciton after photoexcitation on a polythiophene chain.*

There are three methods for introducing electronic excitations onto the chain: chemical doping, photoexcitation across the $\pi$–$\pi^*$ gap, and charge injection in semiconductor device structures. Information about allowed electronic transitions, band gaps and chromic effects is obtained from electronic absorption spectra. Polymers such as PPV, PT and derivatives exhibit readily detected fluorescence. Due to improved preparation methods leading to polymers with

higher purity, the quantum yields of luminescence for several classes of conjugated polymers have been increased to relatively high values [20]. Consequently, there is increasing interest in neutral excitations of the chain. Luminescence from the singlet exciton is found just below the absorption edge, i.e. the emitted light exhibits a Stokes shift. This is a very practical point for light-emission applications, as useful levels of light emission can only be attained at wavelengths that do not result in self-absorption by the polymer.

### 1.3 Substituted conjugated polymers

Due to the rigidity of the polymer backbone, conjugated polymers are intractable and insoluble, which implies that thin-film processing cannot be carried out with these materials. For several conjugated polymers a soluble saturated polymeric precursor can be processed by spin-coating from solution, and converted to the final conjugated form by a thermal treatment [21]. An alternative strategy for polymer processing is to attach flexible side-groups to the polymer chain so that the polymer is directly processable in its conjugated form, and only a single process step is required.

Apart from providing soluble polymers, derivatization with flexible side-groups has shown to have a large influence on the electronic and optical properties and may give rise to a number of interesting phenomena such as thermochromism and solvatochromism [22-25]. Thermochromism implies a reversible change in the electronic spectrum of a material as the temperature changes. For the polymers exhibiting thermochromism reported to date, e.g. poly(3-alkylthiophene)s (P3AT's), the spectrum shifts to higher energies as the temperature is increased and this is universally interpreted to reflect that a conformational change in the side chain induces torsion in the conjugated chain, resulting in disruption of the $\pi$-electron overlap and hence in a decrease of the effective conjugation length. Also, the attachment of flexible side-groups has been shown to induce long-range ordering in the solid state [26] and the occurrence of mesophases [27].

The electronic structure of molecular semiconductors is largely dependent on the chemical structure and this allows tuning of the material properties by attachment of functional groups. For example, substitution with alkoxy groups instead of alkyl groups causes a red-shift in absorption and luminescence as a result of the electron-pushing character of the alkoxy group [28]. The attachment of cyano substituents on the vinylene linkages in poly(*para*-phenylenevinylene) (PPV) causes a red-shift of the luminescence and has been shown to facilitate the injection of electrons in light-emitting diodes, thereby drastically improving the device performance [15].

A promising way to control the luminescence properties of conjugated polymers is to transfer the luminescence properties of well-defined oligomers to polymers by synthesizing alternating copolymers of the $(\text{-A-B-})_n$ type [29-31] (Figure 1.3 a). In such a polymer, the luminescence can be rather precisely controlled through the size and substitution pattern of the active (A) block; the B block is a spacer, preferably selected so as to improve solubility. The study of small model compounds representing the A blocks is expected to provide additional insight into the luminescence process.

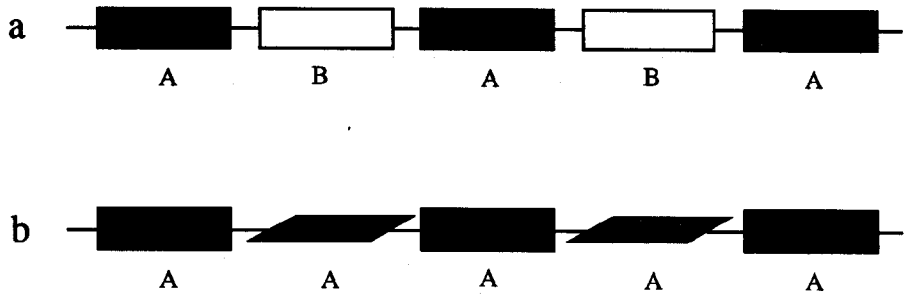
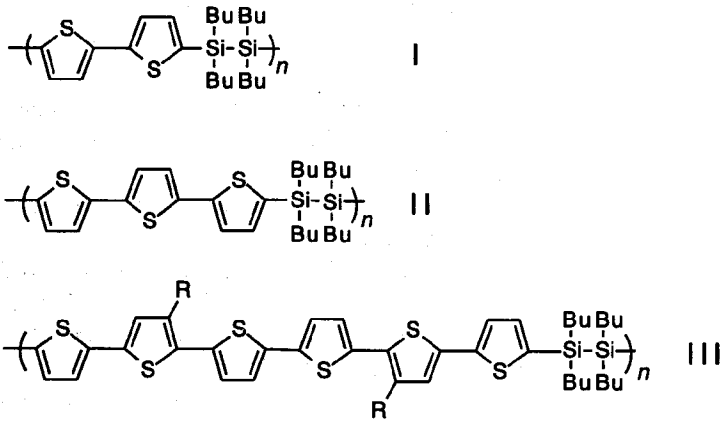



**Figure 1.3** *Two ways of controlling the active chromophore in polymers; A is a conjugated chromophore, B is an interruption unit.*

The alternating copolymers can be designed in a way in which the luminescent chromophores (typically π-conjugated oligomers) are either separated by units with a larger HOMO-LUMO gap, or directly linked to each other in a non-coplanar way as a result of steric interactions between side-chain substituents (Figure 1.3 b). In both structures the conjugation of the main chain is regularly interrupted, giving well-defined, tunable optical properties. This approach is particularly suitable for blue-light emission since this demands short conjugation lengths. The block structure can also enhance the luminescence efficiency through this confinement of excitons in the small gap regions, which hinders their migration to quenching sites [14]. Figure 1.4 shows examples of poly[(silanylene)thiophene] alternating copolymers, which have been used as the active layer in polymer LED devices. Tuning of the luminescence colour from blue to red was achieved by increasing the length of the π-conjugated segments [30].



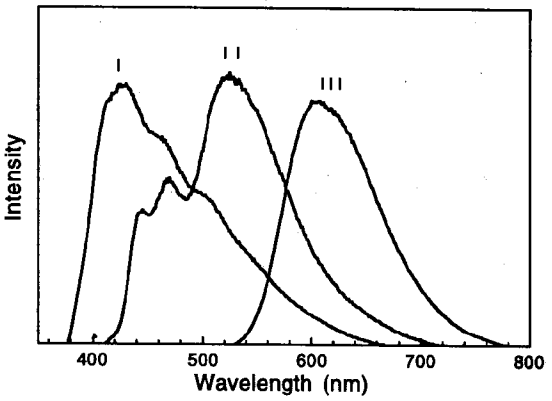



**Figure 1.4** *Chemical structures of poly[(silanylene)thiophene]s with varying length of conjugated segment and the corresponding fluorescence spectra from thin films. R = n-octyl.*

## 1.4 Well-defined oligomers

A useful trend which has emerged in recent years is the use of well-defined oligomers as model compounds for their corresponding polymers [32, 33]. Whereas soluble conjugated polymers are commonly prepared by a polycondensation reaction (either of a bifunctional monomer or by copolymerization of two bifunctional monomers) yielding materials with a certain chain length distribution and usually end-groups in the form of unreacted functionalities, conjugated oligomers can be prepared in a stepwise approach involving monofunctional reactants and yielding materials with a precisely defined chemical structure.

The electronic properties (e.g. the energy of the first absorption maximum in or around the visible range - the optical gap - [34] and the maximum of fluorescence) of oligomers show a steady progression for an increasing number of monomer units, tending towards a limiting value which is taken to be the value of the corresponding polymer. The observed values of such properties of the polymer are often described in terms of "conjugation length", i.e. the length of the oligomer that would have, for the property considered, the same value as the one found experimentally for the polymer. Oligomers are then used as electronic models of polymers and polymer segments. Examples of substituted conjugated oligomers related to PPV which have been reported in the literature, are shown in figure 1.5 [35, 36].

Oligomers are also useful in structural studies. Due to their low molecular weight and precise chemical structure, oligomers can be obtained as macroscopic single crystals [37-41] of which the structural information (molecular geometry and packing) may be correlated to solid-state spectral features. Also, the structural information obtained is useful a guide for determining the thin film structure of those materials.

On the other hand, oligomers are interesting materials by themselves. They can be processed into high purity thin films by vacuum evaporation and devices such as FET's [42] and LED's [43, 44] have been prepared with promising performances. Moreover, inhomogeneities can be detrimental in applications where the individual chains are used for molecular functions: future nanoelectronic or nanophotonic processes will likely require monodisperse materials [45].

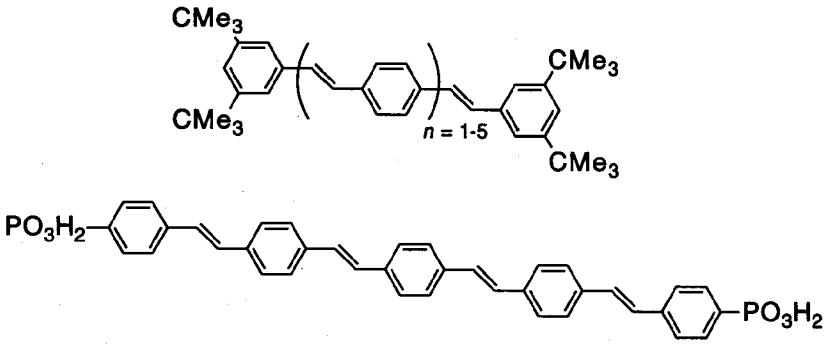



**Figure 1.5** *Examples of substituted oligomers related to PPV.*

## 1.5 Ordered thin films

The electrical and optical properties of molecular semiconductors are directly governed by two factors: the properties of the individual molecules and the spatial arrangement of the molecules within the materials. Fine-tuning of the material properties therefore requires the control of the spatial arrangement of the molecules in the solid state. Insight in intermolecular distances and backbone conformation in the solid state can be obtained from X-ray crystallography and there are examples of conjugated polymers which are available in the form of macroscopic single crystals [46-48]. These materials are the polydiacetylenes (PDA) and their crystallinity follows from a solid-state polymerization of the diacetylene monomer. Macroscopic single crystals of conjugated polymers other than PDA are not available, however.

Efforts that have been undertaken to achieve control of the thin-film structure, can be divided in two classes: techniques which are based on spontaneous organization, and techniques which induce orientation [49-52] such as Langmuir-Blodgett, stretch-orientation and epitaxial orientation. As an example of the former, Garnier *et al.* [53] used the self-assembling properties of α,ω-dihexylsexithiophene to obtain highly ordered films by vacuum deposition onto a Si substrate. From X-ray structural characterization they deduced a highly crystalline structure, in which the molecules are fully extended and oriented almost perpendicularly to the substrate (Figure 1.6). Such films showed an enhanced conductivity in the plane parallel to the substrate as compared to unsubstituted sexithiophene. As an example of the other type of preparation method, Cimrová *et al.* [54] obtained oriented films of substituted PPV by Langmuir-Blodgett deposition, with the conjugated backbones preferentially aligned parallel to the dipping direction. This gave rise to polarized light-emission in LED's prepared from such films.

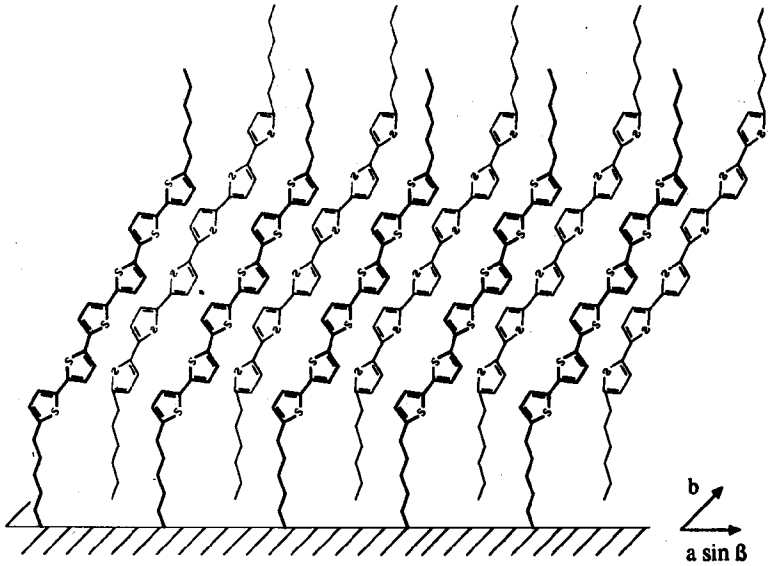



**Figure 1.6** *Schematic representation of the α,ω-dihexylsexithiophene monolayer on substrate, showing two adjacent rows of oligomers along the b-axis (from Garnier et al. J. Am. Chem. Soc., 1993, 115, 8719).*

## 1.6 Electroluminescence

In the case of electroluminescence (EL), the energy associated with an electrical current is converted into light. Fundamental studies have provided a firm basis for the understanding of the behaviour of excited states resulting from excitation by electron and hole injection (for a recent review see [55]). In the EL experiment injection of electrons into the LUMO and holes into the HOMO generates negative and positive polarons, respectively, which migrate under the influence of an electric field and combine on a segment of the polymer chain to form excitons. The basic requirements for an organic layer are that it be an efficient luminescer, a good charge transporter and it must be able of undergoing efficient charge transfer to an electrode. In the following paragraphs each of these phenomena will be discussed in turn.

*Luminescence.* According to spin statistics, a quarter of the excitons initially formed will be singlet excitons which can radiatively decay to the ground state. This decay process is responsible for the observed electroluminescence [12]. The remaining three quarters of the excitons formed are triplets, which for the most part decay non-radiatively. Fluorescence and electroluminescence in typical polymer EL materials are nearly always identical. Excitation

transport along the chains is facile and leads to emission mainly from sequences having the highest conjugation lengths (which are generally in the range of 10 to 15 monomer units). Excitons also move from one chain to another; exciton transfer to "dopant dyes" is sometimes used to obtain other colours [56].

*Charge transport.* Injected charges move by electron transfer reactions (hopping) between molecules [57]. Intrachain transport is expected to be faster than interchain transport, since tunneling through σ-bonds is far more efficient than through space [58]. Nevertheless, the mobility in polymers (~$10^{-4}$ to $10^{-8}$ $cm^2V^{-1}s^{-1}$ for holes) is typically smaller than in molecular glasses (~$10^{-2}$ to $10^{-5}$ $cm^2V^{-1}s^{-1}$). One of the explanations is that conformational disorder along the chain interrupts the ideal one-dimensional transport [59]. The mobility of electrons is even lower and this fact can have important consequences for LED efficiencies as will be explained below.

*Charge injection.* Common cathode materials include Aluminium, Calcium, and others, and anode materials are usually gold and indium tin oxide (ITO). Parker surveyed the different electrode materials and found excellent consistency with a tunneling model in which the barrier for injection was solely determined by the workfunction of the metal ($\phi_w$) and the HOMO and LUMO energy levels of the polymer [60]. Other mechanisms for injection of charges, especially for small barriers, have been proposed by several groups. Surface adsorbates typically give shifts in $\phi_w$ of 0.1 to 1.5 eV and the (chemical) behaviour of the commonly used cathodes evaporated onto conjugated polymers has now been extensively studied [61]. For example, it was observed that Al forms covalent bonds with the polymer.

For highly efficient operation, balanced injection and transport are required. If either of these is not achieved, unproductive (without emission) current is likely to flow and recombination will become localized in a region at, or near to, one of the polymer/electrode interfaces, where quenching effects may be important. To prevent this, a charge transport or injection layer (for either holes or electrons or both) is used in combination with the active layer which can have two effects: (i) it may lower the barrier at the electrode, and (ii) a proper choice of orbital offsets between the layers can block the transmission of the majority carrier, thereby reducing its current and balancing the charge transport.

For all processes that involve the charged species (polaron), viz. injection, migration via diffusion or hopping, trapping, formation of the exciton, and also for the properties that determine the spectral response, viz. the exciton binding energy, HOMO-LUMO energy, and the existence of non-radiative decay channels (quenching), the conformation and packing mode of the molecules (or chain segments) are likely to be of utmost relevance. It is therefore important to obtain detailed structural information of the conjugated polymers which are of interest for their luminescence properties and experimental data that demonstrates relationships between solid-state structural features and spectral behaviour.

The construction of a polymer LED device is illustrated in figure 1.7. A high-work-function metal such as indium tin oxide (ITO), deposited on a glass slide, serves as the anode and is semitransparent at thicknesses of 7-10 nm. After deposition of the conjugated organic material (typically 100-200 nm) a low-workfunction metal is evaporated onto the conjugated material by vacuum deposition. At present, most investigations of EL concern PPV and its

derivatives, P3AT and poly(*para*-phenylene) (PP). One of the great strengths of the organic EL materials is that the emission colour can easily be tuned according to the wide range of organic functional group chemistry, which can be used to modify the chromophore.

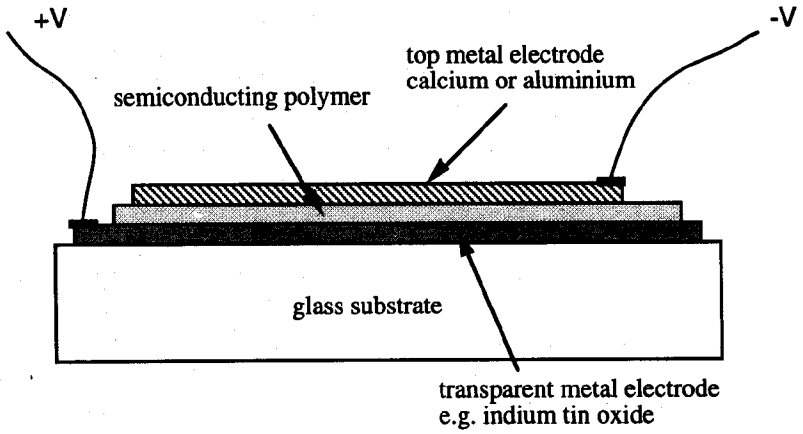



**Figure 1.7** *Schematic representation of a polymer LED.*

## 1.7 Aim and outline of this thesis

Our final goal is the development of new conjugated organic materials, which can be used as the active semiconducting material in thin-film optoelectronic devices [62-68]. Our approach is to synthesize highly fluorescent copolymers in which conjugated segments have a uniform structure and are delimited either by units with a higher HOMO-LUMO gap or by steric interactions of substituents on adjacent aromatic units.

One of our aims is the understanding of the influence of substitution/functionalization on the luminescence properties of conjugated polymers. To achieve this, we systematically vary the chromophore in well-defined polymers and/or oligomers and investigate the influence of different substitutions on spectroscopic properties.

A further aim is to study the influence of solid-state structural aspects like conformation and chain packing on luminescence properties. By growing single crystals of conjugated oligomers, insight in those structural aspects can be obtained. Also, the structural information obtained from single crystals can be used to characterize the structure and molecular orientation of thin (crystalline) films prepared from those oligomers. Eventually, we persue to achieve control of the thin-film structure and the molecular orientation, either based on self-organization of (substituted) organic materials or by other techniques, such as epitaxial growth of thin films. Ultimately this should lead to the establishment of relationships between thin-film structure/orientation and relevant physical (optical/electrical) properties.

**Chapter 2** [69, 70] describes the synthesis of a series of alkylated polythiophenes and discusses the influence of steric interactions between solubilizing alkyl substituents on UV-vis

absorption and fluorescence properties, both in dilute solution and in the solid state. Explanations are supported by spectroscopic data of substituted bithiophenes.

In **Chapter 3** [71, 72] is reported the synthesis of alternating copolymers in which oligo(phenylenevinylene) segments are interrupted by dimethylsilylene units. UV-vis absorption and fluorescence spectra in dilute solution are compared with those of corresponding model compounds and thermal properties are presented. The synthesis of four substituted five-ring PPV-related oligomers (OPV's) is described. The influence of different substitution patterns on spectroscopic properties is discussed.

**Chapter 4** [71, 72] gives the single-crystal structures of two five-ring OPV's and discusses the influence of their substitution patterns on the solid-state structure. Thermal properties of the oligomers are presented.

**Chapter 5** [73] describes the structural characterization by optical microscopy, X-ray diffraction and atomic force microscopy of thin films of the five-ring OPV's prepared by evaporation onto glass in high vacuum. The thin films have been used as the active layer in LED devices. The influence of an annealing treatment on the thin-film structure and LED performance is discussed. UV-vis absorption and fluorescence spectra of the films are compared with the spectra of solutions.

**Chapter 6** describes efforts to control the thin-film structure of three five-ring OPV's [74] and several alkylated oligothiophenes [75] by crystallization onto highly preoriented polytetrafluoroethylene (PTFE) substrates. The degree of orientation is studied by electron diffraction, electron microscopy and polarized spectroscopic measurements.

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